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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: ARO 22681.8-MS-H	2. GOVT ACCESSION NO.: N/A	3. RECIPIENT'S CATALOG NUMBER: N/A
4. TITLE (and Subtitle): Formation of Refractory and Near Noble Metal Silicides by Fast Radiative Processing		5. TYPE OF REPORT & PERIOD COVERED: Final - April 1985-Oct 1988
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Jorge J. Santiago-Aviles		8. CONTRACT OR GRANT NUMBER(s): DAAG29-85-G-0078
9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of Puerto Rico, Physics Dept. Rio Piedras, Puerto Rico, 00931		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: N/A
11. CONTROLLING OFFICE NAME AND ADDRESS: U. S. Army Research Office, Post Office Box 12211, Research Triangle Park, NC 27709		12. REPORT DATE: November 30, 1988
		13. NUMBER OF PAGES: 10
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report): Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Silicides, Metallization Schemes, RTA, VLSI, Tungsten Silicide, Silicon. (mgm)

microohms

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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FORMATION OF REFRACTORY AND NEAR NOBLE METAL SILICIDES BY FAST RADIATIVE PROCESSING

FINAL REPORT

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NOVEMBER 30, 1988

U.S. ARMY RESEARCH OFFICE

GRANT NUMBER DAAG 29-85-G-0078

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STATEMENT OF THE PROBLEM STUDIED.

The technique of fast radiative processing (FRP) was used in the formation of refractory and near noble metal silicides. The processing apparatus consisted of a vacuum or controlled atmosphere reactor and high power quartz-halogen-tungsten lamps supplying radiant energy to the reactor. Radiation from this source provided the driving force for the solid state reaction of a metal thin film with the silicon single crystal substrate. The effect of processing conditions such as maximum temperature, power input, time, temperature gradients, vacuum level or ambient gas was monitored. The processing apparatus itself was characterized and calibrated. The processed silicides were characterized using sheet resistance, x-ray diffraction (XDR), Auger electron spectrometry (AES), secondary ion mass spectrometry (SIMS), optical and scanning electron microscopy (SEM) and backscattering spectrometry(RBS). Information obtained from these experiments was used in a general assessment of the metal thin film - substrate interactions and the fast radiative processing of electronic materials.

SUMMARY OF MOST IMPORTANT RESULTS.

Increasing complexity of device circuitry in recent years in very large scale integration (VLSI) technology has led to the study of refractory metal silicides to replace polycrystalline silicon and aluminum as interconnects and gate metallization schemes. As this trend toward high speed electronics continues, resulting in smaller device sizes, it becomes imperative to find materials with low resistivity and high temperature stability. One of the most promising silicides is the tetragonal phase of tungsten disilicide.

Conventional processing schemes involve the deposition of a thin W layer or the co-deposition of both W and Si in a known stoichiometry, followed by a sintering process to form WSi_2. Regardless of the methods used, the films resulting in the lowest resistivities (30-60 mΩ-cm) were produced when careful attention had been paid to substrate cleanliness and high purity deposition conditions.

Thin films of WSi_2 with resistivities of 30-35 mΩ-cm (among the lowest reported) have been formed by sputter depositing 710A of W metal onto (100) oriented , 3-7 Ω , p-type silicon wafers. The samples were fast radiatively processed in an RTP system under high vacuum for the time anneals ranging from 15-50 seconds at two temperatures (~ 1100°C and ~1150°C). This is a significant reduction in the reaction time of 30 minutes of longer for conventional furnace annealing. The growth process has been shown to be diffusion controlled, with the median grain size correlating with the film resistivity.

Film stresses probably increase with prolonged processing times at high temperatures (~1100°C), which is expected due to the large difference in the thermal expansion coefficients of WSi_2 and Si. As the temperature of reaction is increased (~1150°C),the silicide film finds a means of relaxing the stress by 'buckling' in lieu of rupturing. Furthermore, the high processing temperatures needed to form WSi_2 greatly alter the concentration profiles of the dopant, incorporate oxygen from the annealing ambient and redistribute impurities inherent to the deposition process. Each of these phenomena can change the characteristics of a device; therefore they must become better understood.

This study showed that boron does out-diffuse very rapidly through WSi_2 grain boundaries into the vacuum ambient. However, total loss of boron does not occur during the shortest processing times which still result in high quality films. This implies that a set of RTP conditions exists for maximizing the overall quality of a WSi_2 film. Trace quantities of other impurities has also been detected :F, Cl, Na,K,C, and Cr. Their origin and movement through the growing silicide films have also been monitored as a function of RTP conditions.

The question arises as to why many of the studied phenomena occur simultaneously: completion of the WSi_2 reaction, minimum film resistivity, and the expulsion of oxygen and other impurities. It is at this time that grain boundaries have also grown throughout the films, creating a channel for material diffusion between the WSi_2/Si(100) interface and the vacuum ambient, The advantage of RTP is that since it allows silicides to form so fast, the process can be stopped before all the dopant atoms out-diffuse from the semiconductor substrate.

Nevertheless, the high processing temperatures needed to form WSi_2 can greatly alter the concentration profiles of the dopant redistribute impurities inherent to the deposition processes and incorporate oxygen from the annealing ambient. Each of these phenomena can change the characteristics of a device; therefore, they must become better understood. Secondary ion mas spectrometry (SIMS) has been used to study the resulting dopant and impurity redistributions.

The redistribution of dopant atoms during WSi2 high temperature processing affects important device characteristics such as etching properties, threshold voltage, contact barrier and resistivity. It is notable that the total boron concentration in the samples is reduced as a function of processing time and temperature. The question arises as to where the boron goes after annealing. Most likely, atoms are lost due to fast diffusion through growing WSi_2 grain boundaries and evaporation from the surface, a phenomenon previously observed when the silicide surface is uncapped.

The effect of impurities in refractory metal silicide formation has only been recently reported. These impurities arise as residues left behind from chemical etching solutions (used to clean Si-substrates) or even as impurities present in metal target sources. In a positive SIMS survey from a typical WSi_2 surface, along with tungsten and silicon, the following elements are also detected: hydrogen, carbon, oxygen, sodium, potassium and chromium. In a negative SIMS survey in addition one detects oxygen, fluorine and chlorine. The redistribution of all these impurities were determined as a function of RTP conditions.

Of particular interest is the study of oxygen in the films. The presence of oxygen, when uncontrolled, has only detrimental effects on WSi_2 film growth. By diffusing quickly to the metal-Si interface, the creation of a stable SiO_2 diffusion barrier occurs . This results in raising the temperature needed for silicide formation to ~1100°C. Once this oxide barrier breaks up, uniform WSi_2 films form. Continued heating at these temperatures results in the reduction of SiO_2 atoms from the substrate, forming SiO which is volatile at high temperatures and escapes through the film's growing grain boundaries.

Oxygen is trapped by the W metal during high temperature RTP in high vacuum where ambients are $P < 1.0 \times 10^{-6}$ Torr. This was determined by annealing samples in Penn's UHV thin films chamber where the partial pressure of O_2 is several orders of magnitude less than the RTP system. Consider the oxygen SIMS profiles for two samples, each processed for 30 seconds at 1100°C, with one by RTP and the other by resistive annealing in UHV. In each case, the WSi_2 reaction is completed and both films have low resistivity. However, the total oxygen yield at the WSi_2/Si(100) interface is reduced four-fold in UHV. The gettering of oxygen into the films and its piling at the interface as a function of temperature from 845 to 1100°C is evident in the samples processed in UHV.

The high temperature required for the RTP reaction was necessary to reduce the interfacial oxide barrier. The near elimination of oxygen in UHV allows the W-Si interaction to proceed in a diffusion controlled manner. Auger depth profiles illustrates how dramatically the reaction process for samples annealed at increasing temperature. Furthermore, the growth of W-silicide phases monitored by x-ray diffraction show that no loss of W is observed below 905°C. W metal is then rapidly consumed, completely disappearing by 1050°C. Further evidence explains this loss by showing the growth of the high resistivity tetragonal W_5Si_3 phase above 905°C. At higher temperatures this silicide phase is then consumed, explained by the growth of the low resistivity tetragonal WSi_2 phase. Here it is observed that WSi_2 also begins to form at temperatures above 905°C, first at the expense of W-metal, then of W_5Si_3, up to 1100°C.

This pattern of growth (seen by both AES and XRD): W metal to W_5Si_3 to WSi_2, is expected since it is known that in the absence of an interfacial oxide diffusion barrier the kinetics of reaction are diffusion controlled with Si as the moving species. This is usually accomplished by capping the W film with a few hundred angstroms of Si. In Penn's case, oxygen was simply kept out of the annealing ambient by the use of UHV as seen by SIMS.

Obviously the use of a UHV chamber for the annealing process removes the need for the technology required by RTP by gaining control of the annealing ambient. Understandably, the next step forward involves a completely in-situ UHV film deposition and annealing process. Such experiments have already been successfully accomplished for YSi_{2-x}(0001)/Si(111) structures, resulting in a highly reproducible growth mechanism. Films of the highest quality and cleanliness have been produced, as determined by electrical, structural and impurity level measurements.

Epitaxial $YSi_{2-x}(0001)/Si(111)$ formed by vacuum annealing sputter deposited Y-metal has an RBS minimum channeling yield Chi(min) = 8%, making it one of the best known epitaxial silicides. Yttrium silicide has the hexagonal AlB_2 structure which has a 0.0% lattice mismatch with Si(111). In this study, 300 A Y-metal is deposited onto Shiraki cleaned Si(111) substrates by electron beam evaporation in a UHV thin films growth and analysis chamber with a base pressure < 1.0×10^{-10} Torr. The samples were then in-situ resistively annealed for 20 minutes for temperatures ranging from 527°C to 920°C. During both deposition and annealing, the vacuum ambient rose no higher than 1.0×10^{-9} Torr. Auger electron spectroscopy indicates the presence of only Y and Si, with no elemental impurities detectable above the background. The YSi_{2-x} films (now ~ 425A thick) formed at temperatures above 650°C gave hexagonal 1x1 LEED patterns, indicating a high degree of structural order.

The reaction between a Y-film and an Si(111) substrate is known to nucleate at 480°C. We find this is correct, however, a YSi_{2-x} film's properties vary strongly with annealing temperature. At 810°C, sheet resistance has a minimum value, while x-ray diffraction shows the epitaxial (0001, 0002) YSi_{2-x} peak heights to be at a maximum. SIMS depth profiles show the presents of only trace quantities of O, C, F, Cl, Na and K. The relative concentrations of these impurities varies neither in depth nor from sample to sample. These results indicate that higher temperatures (> 480°C) are needed to anneal out defect structures, consequently improving both film epitaxy and conductivity.

We have explored the deposition of refractory metal silicides from organometallic precursors. The organometallic compound silyl - Ta - carbonyl, is a stable, low vapor pressure liquid at room temperature which facilitates its deposition by the technique of spin-casting. The silyl - metal - carbonyls readily disproportionate under static pyrolysis conditions and it is known that the most important fragmentation pattern involves stripping of H and CO leaving abundant $[M_xSi_y]^+$, and Si atoms. Static pyrolysis of these organometallics, quite unstable in the presence of moisture, is known to yield polycrystalline agregates of Fe- Si compound with large amounts of carbon and oxygen. To avoid these difficulties we have constructed a small flow pyrolysis system. This system incorporates rotameters and RTA for thermolysis and /or photolysis of the precursors. We have achieved near stoichiometric deposition at temperatures as low as 700°C for the tantalum material but the resulting polycrystalline aggregate is mixed phase with extensive carbonate incorporation.

The student exchange program between the University of Puerto Rico's physics department and the Moore School of Electrical Engineering of the University of Pennsylvania, sponsored largely by this grant has been very successful. With the collaboration and resources from the National Science Foundation and private industry we have been able to exchange two graduate students. One of them, Juan Carlos Delgado from Puerto Rico spent several weeks participating in silicide research (RTA of $PdSi_2$) with his peers at Penn and probing the environment of a research oriented University. The other student from the continent, Michael Siegal, spent several weeks at the University of Puerto Rico doing research work on silicides (SIMS of RTP WSi_2) and learning of another culture, the efforts of the Puerto Ricans in upgrade the quality of the academic scientific enterprise and the importance of grants such as the one from ARO, in making this possible.

The other group was comprised of a Puerto Rican undergraduate, (Rudy Rivera) who spent a summer period (10 weeks) working as an aid to one of the graduate students doing silicide work. His travel to Philadelphia was supported by NSF and Ford Motor Co. Another member of the second group was an instructor from one of the four year colleges of the University of Puerto Rico, He is a former student of mine with an M.S. in physics from UPR's main campus. He was my collaborator in silicide research (Stress measurements in tungsten silicide thin films) for several weeks. His travel to Philadelphia was sponsored by NSF. My graduate student, Mike Siegal returned to Puerto Rico in May 1988, doing more SIMS work with WSi_2 films annealed in UHV and with UHV annealed and deposited YSi_2 ultra-thin films. This exchange more than most programs, provides the needed motivation for the Puerto Rican students to consider science and engineering as a viable and exciting alternative for a rewarding professional life.

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1. "Characterization of Tungsten Silicides Formed by Rapid Thermal Annealing", M. Siegal, J.J. Santiago and J. Van der Spiegel, Materials Research Society Symp. Proc., Vol. 52 (1986).

2. "The Influence of Interposed Ti Thin Film on the Formation of Tungsten Silicide", C.S. Wei, M. Setton, J. Van der Spiegel and J.J. Santiago, Journal of Applied Physics, 61,4, 1429 (1987).

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LIST OF ALL PARTICIPATING SCIENTIFIC PERSONNEL SHOWING ANY ADVANCED DEGREE EARNED BY THEM WHILE EMPLOYED ON THE PROJECT.

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